Synthesis and Characterization of

Ferroelectric Polymer Ceramic Composites

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Master of Science

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DECLARATION

I hereby declare that the work carried out in this thesis is entirely original. It was carried out by me at Department of Physics and Astronomy, National Institute of Technology, Rourkela.

I further declare that it has not formed the basis for the award of any degree, diploma, or similar title of any university or institution.

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CERTIFICATE

This is to certify that the thesis entitled **"Synthesis and Characterization of Ferroelectric Polymer Ceramic Composites"** being submitted by **Manaswini Kar** in partial fulfilment of the requirements for the award of the Degree of Master of Science in Physics at National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

Date: Dr. Dillip Kumar Pradhan

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Date: Manaswini Kar

Dedicated to my parents

Whose love has contributed

So much for my strength and faith

ABSTRACT

Ferroelectric polymer-ceramic composites were prepared by the solution casing technique usingpolyvinylidenefluoride (PVDF) as polymer matrix and $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) as the ceramic powder. The concentration of NBT has been varied with respect to polymer host. The formation polymer composites have been confirmed by the X-ray Diffraction (XRD) analysis. The presence of both the crystalline and amorphous phases has also been observed from XRD pattern. Fourier transform infrared spectroscopy (FTIR) confirms the presence of vibrational bands of both the phases in the composite. The microstructure/surface morphology of the polymer-ceramic composites was analysed by the optical microscopy.Dielectric properties of the composites have been studied with the variation of frequency at room temperature.

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CHAPTER-1

INTRODUCTION

In the recent years, material scientists are putting lots of interest for the development of new multifunctional ceramic, polymer, polymer composite materials for many device applications in electronics and optoelectronic industry [1]. In view of the above, polymer composites, in general, and ferroelectric polymer-ceramic composites, in particular, have received a significant attention in view of their technological importance in devices such as high energy density capacitors, sensors, actuators, transducers etc. [2].The fabrication of composites is to combine two or more different materials/phases having different properties to obtain the suitable material properties that often cannot be obtained in single-phase materials. In the context of energy storage device, ferroelectric ceramic polymer composites have been studied world-wide [3].

The electric energy density can be given by the relation $U = (\varepsilon_r E_b^2)/2$, where ε_r is the dielectric constant or permittivity of the material and E_b is the breakdown strength. For higher electric energy storage, both large permittivity and high breakdown strength are required. Ceramic materials possess larger permittivity but smaller breakdown strength. They are stiff and brittle in nature, which is barrier for flexibility. Polymers possesssmaller dielectric constant and larger breakdown strength. Polymers are flexible in nature also. So by combining the larger dielectric constant of ceramics and higher breakdown strength of the polymers we can obtained the desirable property for energy storage application.

FERROELETRICS PHENOMENA

The phenomena in which spontaneous polarization occurs even in the absence of external field is called Ferro electricity. If the crystals exhibit Ferro electricity, then the crystal is said to be ferroelectric crystal.In this case, the centre of +ve and –ve charge doesn't coincide with each other in the absence of the electric field thus leading to a non-zero value of the dipole moment [4, 5].

There are 32 point groups in crystal structure.Again they belongs to either centric or non-centric class.Out of the 32 point groups 11 crystal classes are centre of symmetric and the rest 21 are non-Centrosymmetric.Out of the 21 non-centricpoint group 20 point groups show piezoelectric and one is in non-piezoelectric group (432).Again out of the 20 piezoelectric point groups 10 groups have a unique polar axis and thus they exhibitpyroelectric effect.As it is well know that the polarisation is a function of temperature,if the polarization change by changing the temperature, then it is called pyro electrics. Ferroelectric crystals are the special call of pyro electric family, which possess additional property i.e., the direction of spontaneous polarization can be reversed by the application of electric field. The classification of 32 point group according to according to the above classification is given below [6].

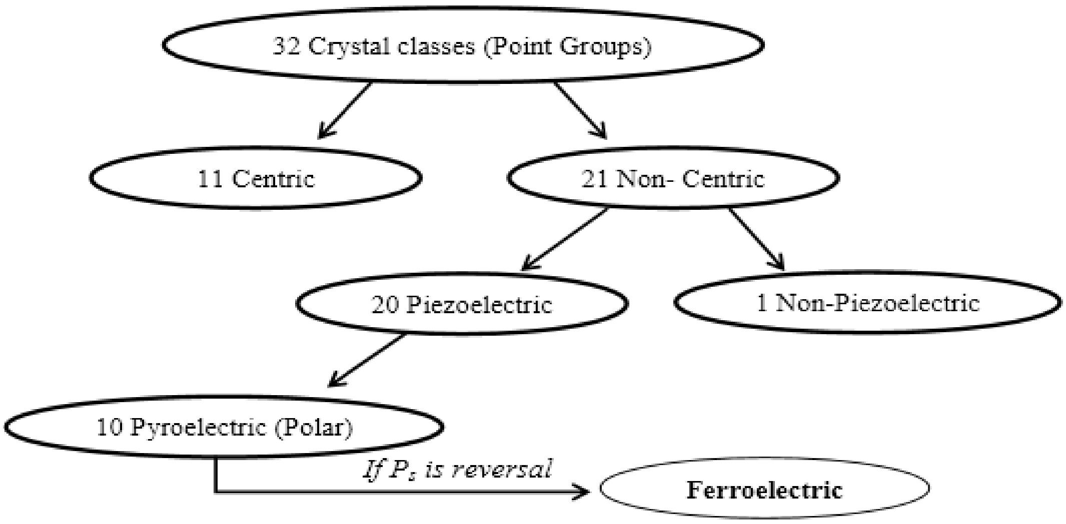


Fig. 1Classification of 32 crystallographic point groups

The variation of polarisation with electric field is not linear and it gives a closed loop called the hysteresis loop, which is the typical siganture of ferroelectric materials as shown in Fig. 2. In side of a ferroelectric crystals, ferroelectric domains (ferroelectric region) are separated by domain wall.

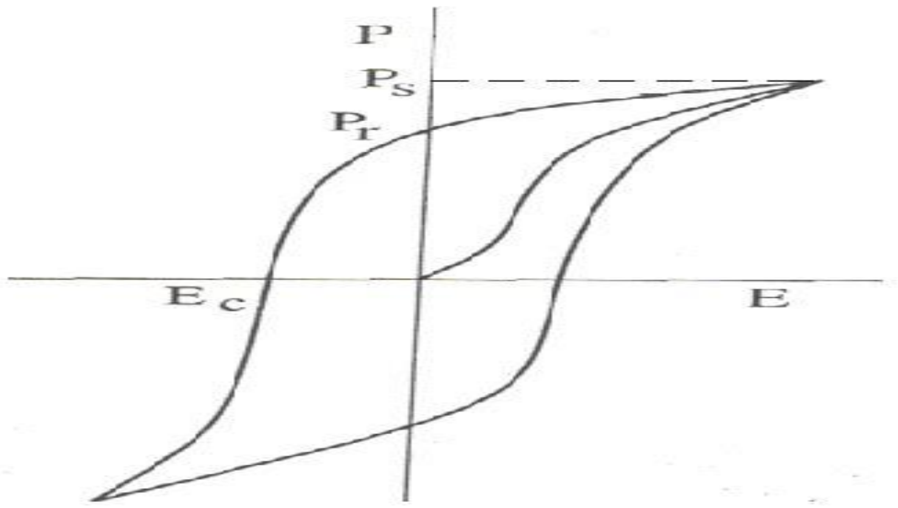


Fig. 2 Ferroelectric Hysteresis loop for a ferroelectric crystal [4]

All ferroelectric material undergoes a ferroelectric phase transition at aparticular temperature known as Curie temperature (T_C). At temperature $T > T_C$, the crystal does not exhibit ferroelectric properties, while for $T < T_C$ it showed the ferroelectric properties. If we decrease the temperature through the Curie temperature, then there will be a phase transition from a non-ferroelectric phase (i.e., paraelectric phase) to a ferroelectric phase. The temperature dependence of the dielectric constant above the Curie point ($T > T_C$) in ferroelectric crystals is governed by the Curie-Weiss law $= C/ (T-T_0)$, where C and T_O are the Curie-Weiss constant and Curie-Weiss temperature, respectively.

FERROELECTRIC CERAMICS AND POLYMERS

After the discovery of ferroelecticity in $BaTiO_3$ ceramic oxide, a large number of oxides with different structural families such as perovskite, tungsten bronze, and pyrocholore have been investigated extensively. Among all, the widely studied ferroelectric materials belong to perovskite structure. Some of the widely studied ferroelectric materials belongs to perovskite structure are lead titanate ($PbTiO_3$), lead zirconatetitanate (Pb (Zr_xTi_{1-x}) O_3 or PZT), lead lanthanum zirconatetitanate ($Pb_{1-x}La_x(Zr_yT_{1-y})_{1-x/4}O_3$ or PLZT), and lead magnesium niobate-lead titanate (Pb $(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$, or PMN-PT). It is well know that lead is toxic and causes serious environmental concern. So scientific community dedicded to use lead free devices. Therefore, enormous effort has been made to develop alternative lead-free ferroelectric materials due to the toxicity of lead and concern for environmental protection. Among the various ferroelectric ceramics $Na_{0.5}Bi_{0.5}TiO_3$ is lead free ferroelectric ceramic oxides showed relatively good ferroelectric properties.BNT is ferroelectric with Curie temperature, T_c ~ 320^0C (with diffuse phase transition), remenant polarization P_r ~ 38 $\mu C/cm^2$, and coercive field E_c ~ 73kV/cm at room temperature.

Ferroelectric poly(vinylidene fluoride) (PVDF) and its copolymers, such as poly(vinylidene fluoride-co-trifluoroethylene) [P(VDF-TrFE)] and poly(vinylidene fluoride-co-hexafluoropropylene) [P(VDF-HFP)], have been mostly utilized in the formation of the dielectric composites, owing to their relatively high dielectric permittivity as compared other polymer matrix **[7].** For the fabrication of composite materials, we need a ferroelectric polymer and a ferroelectric ceramics oxide so that we will get the required properties. In the present case we have taken poly (vinylidene fluoride) (PVDF) as polymer host and $Na_{0.5}Bi_{0.5}TiO_3$ as ceramics oxides.

LITERATURE REVIEW

There are a great deal of research been carried out on ferroelectric polymer ceramic composite. T. Hu, J. Juuti, H. Jantunen, Taisto, fabricated the composite of barium strontium titanate (BST) and thermoplastic cyclic olefin copolymer with different BST loadings using common and nanosize ceramic powders. They reported that the relative permittivity and loss tangent of the composites are gradually increased as the volume fraction of BST was increased [8]. J. W. Perry et.al. Prepared high-quality dielectric nanocomposite using phosphoric acid modified $BaTIO_3$ and ferroelectric polymer (PVDF-HFP) by simple solution-processing techniques. They reported that the nanocomposite exhibit a remarkable combination of high dielectric constant and large dielectric strength, yielding a high energy-storage capacity [9, 10].Q. Wang et. al. prepared polymer nanocomposite based on the surface-functionalized $BaTiO_3$/TiO_2 nanoparticles and ferroelectric polymers. They reported that the presence of organic surface layers on the particle affords excellent compatibility between the fillers and the polymer matrix and ensures uniform composite films even at higher filler concentrations. They also demonstrated the dominant role of dielectric permittivity of the polymer matrix in determining the energy density of the nanocomposite [11, 12].Z. M. Dang et. al. prepared PVDF based nanocomposite using surface hydroxylated$BaTiO_3$ nanoparticles as filler. They reported that the surface functionalized nanocomposite showed lower loss tangent and higher dielectric strength as compared to pure nanocomposite [13]. P. K. C. Pillaiet. al. have studied the pyro electric, and conductivity behaviour in PLZT/$BaTiO_3$ and PVDF composites [14]. R.P. Tandonet. al. have synthesized and characterized ferroelectric materials based on PZT, PMN and polymer ceramic composites for hydrophones and other underwater devices. They are also investigating the dielectric properties of ceramic resonators [15]. S. Sen et. al. synthesized and characterized ferroelectric polymer nanocomposite based on polymer (PVDF) polymer and ferroelectric nanoceramics ((0.65PMN–0.35PT)) [16].

MATERIALS UNDER PRESENT INVESTIGATION

Based on the literature the materials under present investigation arePVDF-NBT ($Na_{0.5}Bi_{0.5}TiO_3$) Composites with different concentration of NBT

OBJECTIVES OF THE THESIS:

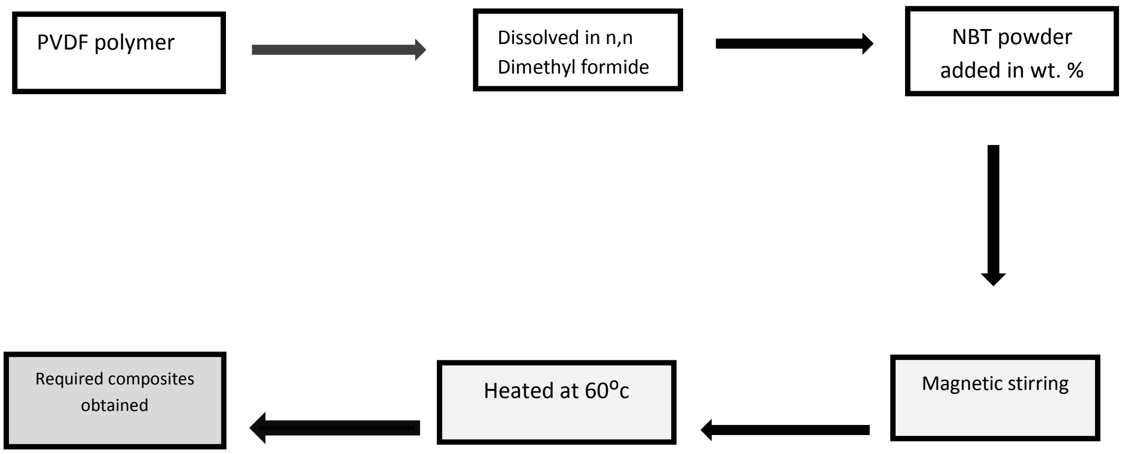
Basing upon the importance of the ferroelectric–ceramic composites the objectives are as follows:

- Synthesis of PVDF-NBT composites by solution casting method.
- Formation and structural characterization of the composites by X-ray diffraction technique.
- Vibrational characterization by using FTIR technique.
- Surface morphology studies using optical microscope.
- Studies of the dielectric properties with frequency at room temperature.

CHAPTER-2

SYNTHESIS OF PVDF-NBT COMPOSITES USING SOLUTION CASTING TECHNIQUE:

PVDF-NBT composites were prepared using solution casting technique. At first 1g of NBT was taken in a crucible and heated it for two hours with a temperature of 150ºC.Then the powder was grinded for 30 mins. Then 30ml of N, N-Dimethylformamide was taken in a conical flask and 1g of PVDF was added to it. The mixture is left at ambient temperature for 12hrs under continuous magnetic stirring. Then to the above mixture stoichiometric (0g, 0.1g and 0.3g) amount of ceramic powder (NBT) was added. Again the mixture was stirred for 3hrs and a homogeneous mixture was obtained. Then the homogeneous mixture was casted on glass petridish and heated in a hot air oven at 60ºC for 4-5 hours. Finally the polymer film was obtained.



Flow chat for the polymer-ceramic films

CHARACTERISATION TECHNIQUES:

X-RAY DIFFRACTION (XRD)

Here XRD was carried out using RigakuUltima IV diffractometer with $Cu\ K_{\alpha}$ radiation ($\lambda =$ 1.54056 Å). The scanning range was chosen from 10° to 45° with scanning rate 2° per minute and 0.002° step size.

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Infrared vibrational spectroscopy is a most common technique for structural elucidation and compound identification. FTIR Spectra of the prepared samples were recorded from range of wavenumber $400\ cm^{-1}$ – $800\ cm^{-1}$
with the help of Thermo Nicolet, NEXUS – 870 Infrared spectrometer at room temperature

OPTICAL MICROSCOPY

Optical microscopy for particle characterisation can generally be applied to particles 1µm and greater. The optical microscopy had been carried out using Leica DFC 295 microscope with different magnifications at room temperature.

DIELECTRIC STUDY

The dielectric impedance spectroscopic were studied using PSM 1735 Impedance analyser of Newton's 4th Limited, UK. The chosen frequency range for investigation was 1Hz to 1MHz at room temperature. The data were recorded with input perturbation signal of 500 mV.

CHAPTER-3

RESULT AND DISCUSSION

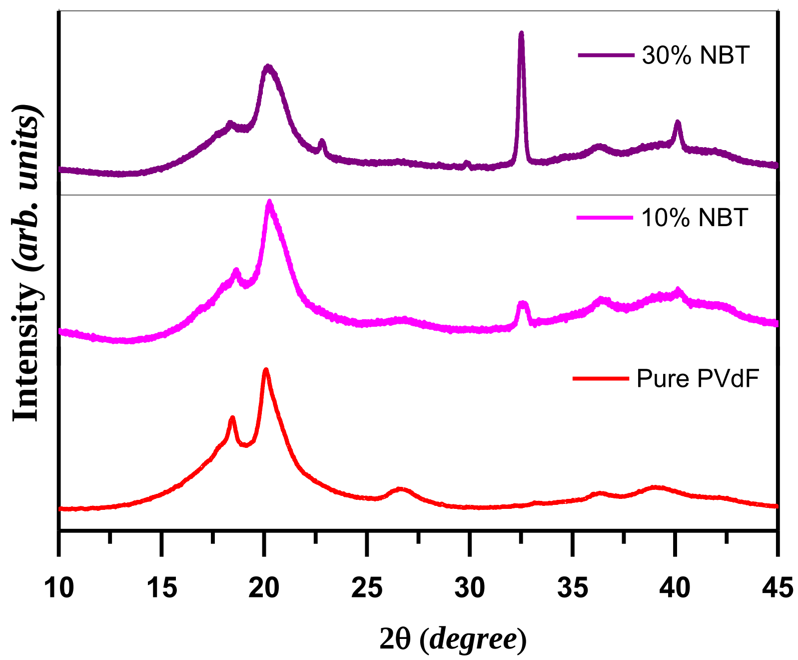


Fig.1. X-ray Diffraction pattern of polymer-ceramic composites

Fig. 1.shows the XRD pattern of the polymer-ceramic composites at room temperature.From the XRD pattern, it is observed that, the pure PVDF pattern is characterised by the existence of both crystalline peaks and the humps indicating the presence of both crystalline and amorphous region (i. e., semi-crystalline nature). When NBT has been added, the presence of NBT peak around 32^0 is observed. The NBT peak is more prominent with increase in NBT content. The presence of both the polymer and ceramic peaks in the XRD pattern suggesting the formations of the composites.

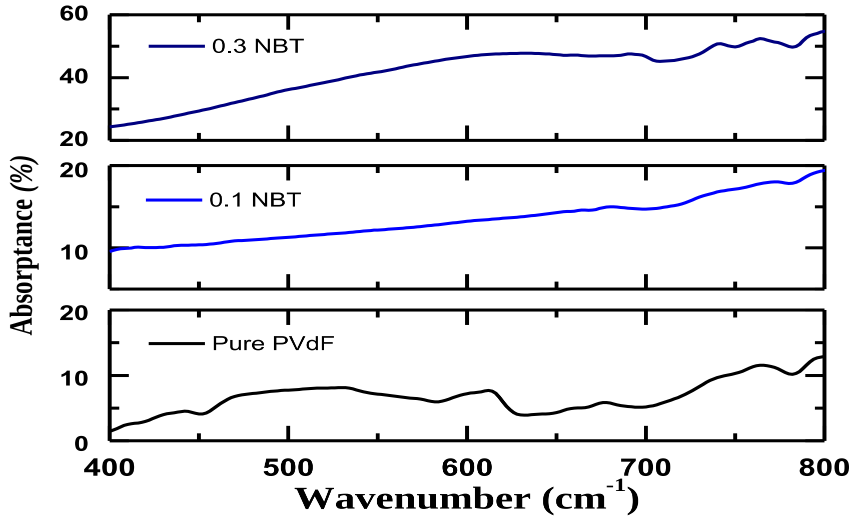


Fig.2 FTIR spectrum of polymer-ceramic composites

The FTIR spectra of the polymer ceramic compositesare shown in Figure-2. From the spectra, it is observed that in case of pure PVDF, the vibrational bands corresponding to PVDF is present and after addition of NBT, the vibrational bands of PVDF and NBT are present. This suggest the formation of the composites.

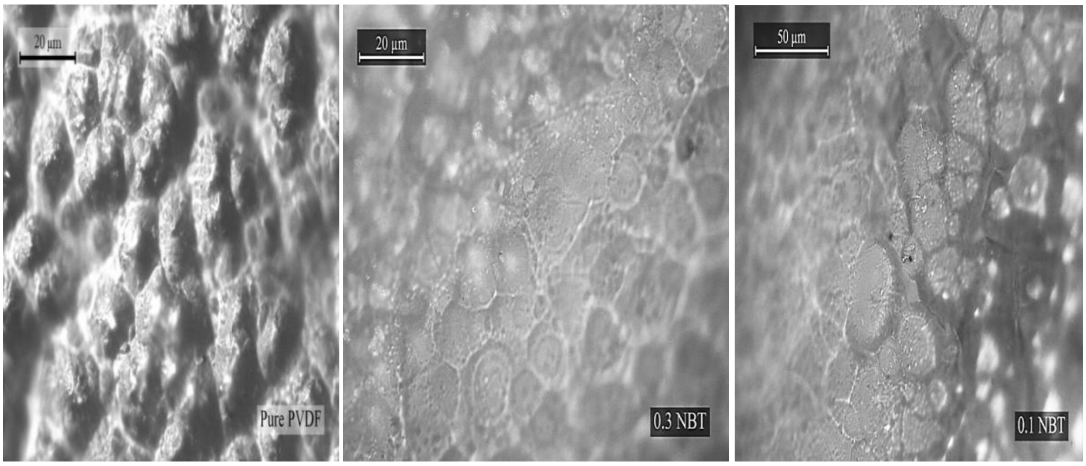
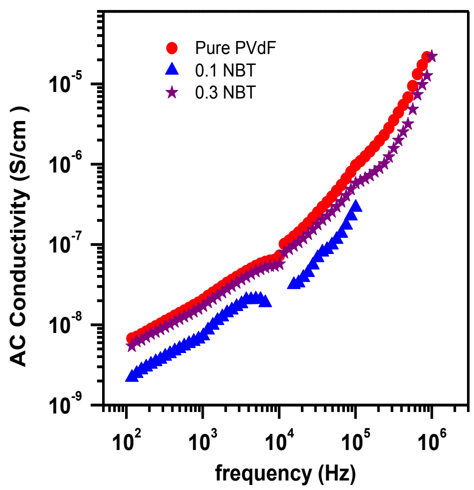


Fig.3 Optical micrographs of polymer-ceramic composites

Figure-3 shows the optical micrographs of the polymer-ceramic composites. The micrographs are characterized by the presence of spherulites separated by the boundary. The spherulites are are crystalline nature and the boundary are amorphous nature. The presence of both the crystalline and amorphous content suggesting the semi-crystalline nature of the composite.



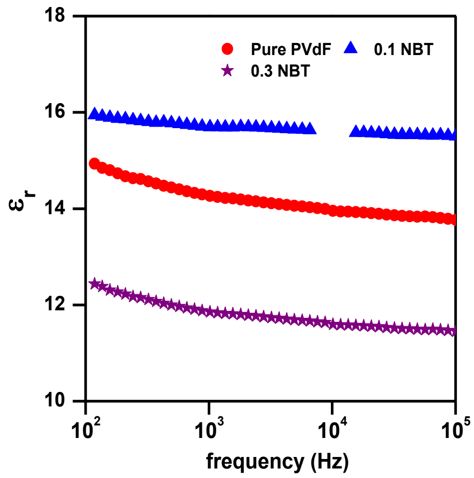


Fig.4 (a) AC conductivity vs. Frequency (b) ε_r vs. Frequency

The dielectric properties of the polymer-ceramic composites have been carried as a function of frequency at room temperature as shown in Fig. 4. From figure it is observed that, the ac conductivity increases with the increase in frequency, whereas the dielectric permittivity decreases with the increase in frequency. The decrease of dielectric constant with increase in frequency is due to the polar nature. The maximum value of dielectric constant is found for 10% NBT.

CONCLUSIONS

In the present work the PVDF-NBT composites were prepared by the solution casting technique.The Structural characterization has been done by the XRD, the micro structural characterization has done by the optical microscopy and the vibrational characterization by the FTIR spectrometer.The dielectric study of the samples has been carried out using the impedance analyser.

Based on our results, the following conclusions have been drawn.

- ✓ Polymer composites were prepared by solution casting technique.
- ✓ The formation of the polymer composites were confirmed by XRD analysis. Pure PVDF as well as composites shows the presence of both crystalline and amorphous phases.
- ✓ Optical micrographs show the presence of spherulites separated by the grain boundary suggesting the semi-crystalline nature.
- ✓ FTIR confirms presence vibrational bands of both the phases.
- ✓ Dielectric permittivity decreases with increase in frequency. The maximum value of dielectric constant is found for 10% NBT.
- ✓ AC conductivity increases with increase in frequency.

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